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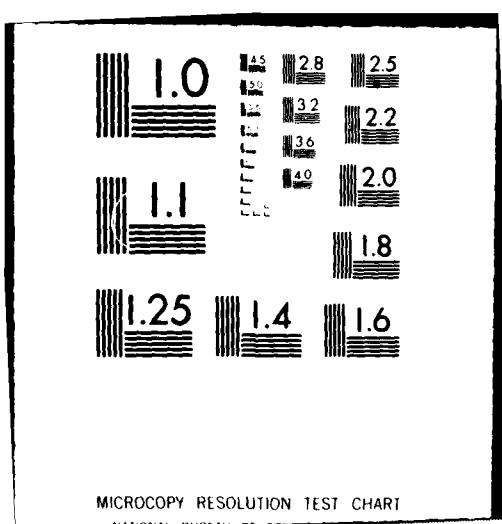
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STUDIES IN THE IDENTIFICATION OF HYDROCARBON PRODUCTS IN WASTE--ETC(U)
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6 STUDIES IN THE IDENTIFICATION
OF HYDROCARBON PRODUCTS IN WASTEWATER

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INTRODUCTION

At Army installations, operations essential to the maintenance, servicing, and cleaning of wheel- and track-type vehicles produce large volumes of wastewater which may contain variable concentrations of hydrocarbon products used in the servicing and cleaning operations. Federal regulations require the monitoring of hydrocarbon concentrations in effluents discharged into waterways; and regulatory agencies such as the Environmental Protection Agency are vested with authority to assess liabilities for restoration costs in cases of environmental pollution by outfalls exceeding established concentration limits.

Methods of quantification of "total hydrocarbons" have been developed and approved by EPA and provide the basis for the monitoring of this class of environmental pollutant (1,2). However, while these methods provide essential data on hydrocarbon concentrations in effluent samples, they do not provide information needed for identification of the specific hydrocarbon products present in the effluent to aid in tracing a given hydrocarbon pollutant to its source for preventative action.

Extensive R&D efforts by other agencies and independent groups have been directed to the identification and classification of petroleum oils. A variety of analytical techniques have been employed, including infrared spectroscopy, absorption and fluorescence

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spectrophotometry, gas and liquid chromatography, and trace-elemental analyses. Reviews and investigations of applications of these techniques are reported by Adlard (3), Bentz (4), Brown et al. (5), Gruenfeld (6), Kawahara (7), and Wilson et al. (8). A comprehensive current review of the state of the art in oil-spill identification, including remote-sensing methods, was presented by Bentz (9).

The general focus of the reported research has been on identification ("fingerprinting") for forensic purposes of a crude oil or petroleum derivative occurring as a single component in an accidental or clandestine marine spill. Former studies have not been concerned with identifying specific hydrocarbon products occurring as multiple components of complex mixtures as would be found in wastewater effluents.

OBJECTIVE

The objective of this study was to develop a readily usable analytical method for the identification of specific hydrocarbon products in wastewater from vehicular service and wash-rack areas at Army installations.

The hydrocarbon products to be included for identification in this study were to be limited to the following MIL-Spec products employed in the servicing and maintenance of military vehicles: Motor Oil, Diesel Fuel, Hydraulic Fluid, Brake Fluid, and Solvent Type II.

APPLICATION OF INFRARED SPECTROSCOPY TO OIL IDENTIFICATION

For more than three decades, infrared spectroscopy (IR) has been used extensively to characterize the composition of petroleum constituents. In the early development of methods for the "fingerprinting" of oil-spill samples, IR provided a direct means for identification through visual comparison of the IR spectrum of a recovered oil spill sample with a library of reference spectra of oils of known origin.

The advent of commercially available IR spectrophotometers with digitizing capability, and the application of computer interfacing has opened the way for the use of statistical methods of data reduction to replace the earlier, subjective visual-comparison techniques.

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In the pattern-recognition method developed by Lynch and Brown (10), log-ratios of absorptivities of an unknown oil sample to a reference oil, at each of 21 selected absorption peaks, are used to obtain a single numerical value which is a measure of the overall difference between the unknown sample and the reference oil. The multivariate statistical approach to the fingerprinting of oils developed by Mattson *et al.* (11,12) has introduced statistical probability functions in describing the extent of match or mismatch between the IR spectrum from the oil spill sample with a computer file of reference spectra of petroleum oils of known origin.

In another computer-oriented fingerprinting method described by Killeen *et al.* (13), a digitized IR spectrum is treated as a vector in n-dimensional space; and the closeness of fit to the hyperplanes generated by an unknown oil and a reference oil is a measure of overall difference.

THE ANALYTICAL PROBLEM DEFINED

The analytical objectives and associated problems in fingerprinting oil-spill samples are distinctly different from those in identifying the presence of specific hydrocarbon products as components in a mixture of hydrocarbons. Fingerprinting a given oil sample involves the use of a set of variables (absorption bands in IR spectroscopy) to test whether the spectrum of an oil-spill sample corresponds, at a high statistical confidence level, to one in a computer file of reference oils of known origin. Differences between the infrared spectra may be very subtle, and small variations in intensity ratios between a myriad of peaks must be determined with high precision and accuracy.

Identification of hydrocarbon products in a mixture of petroleum-derived hydrocarbon products (each of which is a mixture of hydrocarbons) involves the use of an appropriately selected set of absorption bands to test for the presence (above a given discriminator value) of specific hydrocarbon products on the basis of the reference spectra of the individual products. The absorption spectrum of the mixture to be analyzed is a summation of the absorption spectra of the individual hydrocarbon products present; and the analytical problem consists of "unscrambling," or differentiating the integrated signals to the extent that individual hydrocarbon products in the mixture can be identified.

DEVELOPMENT OF THE ANALYTICAL METHOD

In a system in which five specific hydrocarbon products in an effluent are to be identified but not quantified, analytical requirements might be met through the use of a simple binary information format based on the presence or absence of absorption peaks unique to each hydrocarbon product--if an adequate number of such peaks for each product could be found that are analytically suitable.

On that supposition, scans of absorption spectra of the five hydrocarbon products were made on a computer-interfaced Perkin-Elmer 283B spectrophotometer (Figures 1 through 5). Digitized spectral information of each product was simultaneously stored on magnetic discs. Peak tables listing the wavenumber of each absorption peak with the corresponding absorbance value were computer generated for each of the five referenced hydrocarbon products; and a compilation of the wavenumbers of the recorded peaks for the five hydrocarbon products was assembled.

Since the hydrocarbon products were all of petroleum origin, the major and secondary absorption bands were in common to all five products. Absorption bands that were not in common to the five products were relatively weak--some barely above background noise. The intensities of the very weak peaks were then computer enhanced by accumulating and averaging five successive spectral scans. This process significantly improved the signal-to-noise ratio of these peaks because baseline noise, being random, tends to average to zero, whereas true absorption signals occur in only a positive direction.

Peaks in common with more than two hydrocarbon products were eliminated from further consideration; the wavenumber values of the remaining peaks and the corresponding hydrocarbon products represented by each peak are listed in Table 1. A tabulation from Table 1 of the number of absorption bands unique to each hydrocarbon product, and of the number of bands shared between two products, gave the following scores:

<u>Product</u>	<u>Bands Unique to One Product</u>	<u>Bands Shared Between Two Products</u>
30W Motor Oil	4	5
Diesel Fuel	6	5
Hydraulic Fluid	8	2
Brake Fluid	4	6
Solvent Type II	0	4

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TABLE 1
INFRARED ABSORPTION BANDS UNIQUE TO TWO OR LESS HYDROCARBON PRODUCTS

Absorption Band (cm ⁻¹)	30W Oil	Diesel Fuel	Hydraulic Fluid	Brake Fluid	Solvent Type II	Frequency of Occurrence
1952				x		1
1775	x					1
1734			x			1
1717		x				1
1706	x					1
1690		x				1
1325				x	x	2
1297				x		1
1269			x		x	2
1248				x		1
1240			x			1
1227	x					1
1207	x					1
1157		x			x	2
1150			x			1
1115				x		1
1092		x				1
1077	x	x				2
1070				x	x	2
1064			x			1
1031	x	x				2
1014	x		x			2
945	x	x				2
865	x	x				2
851			x			1
805		x				1
775			x			1
747			x			1
739		x				1
699		x				1
634			x			1

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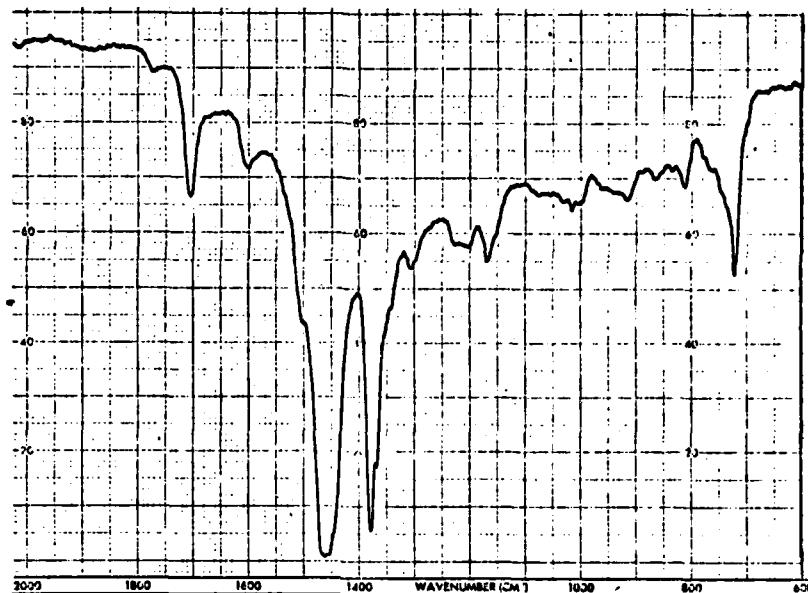


Figure 1. Infrared Spectrum of 30W Motor Oil

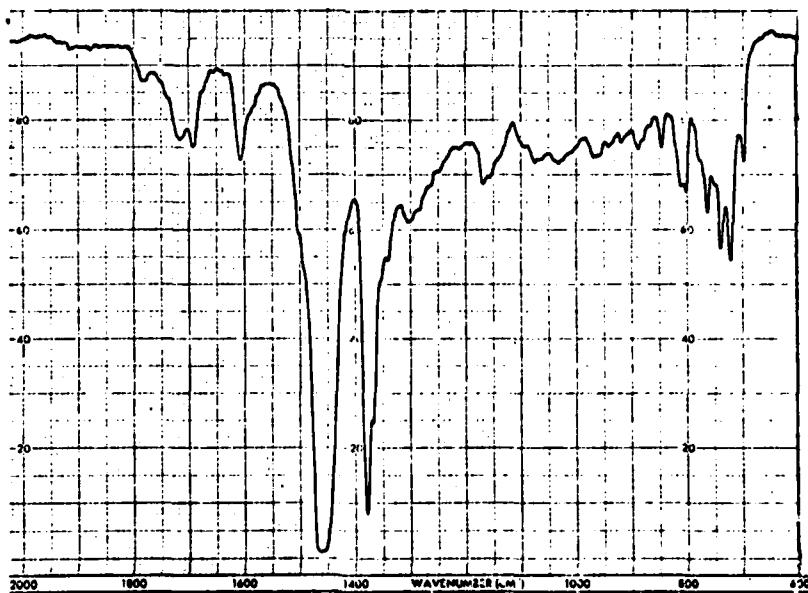


Figure 2. Infrared Spectrum of Diesel Fuel

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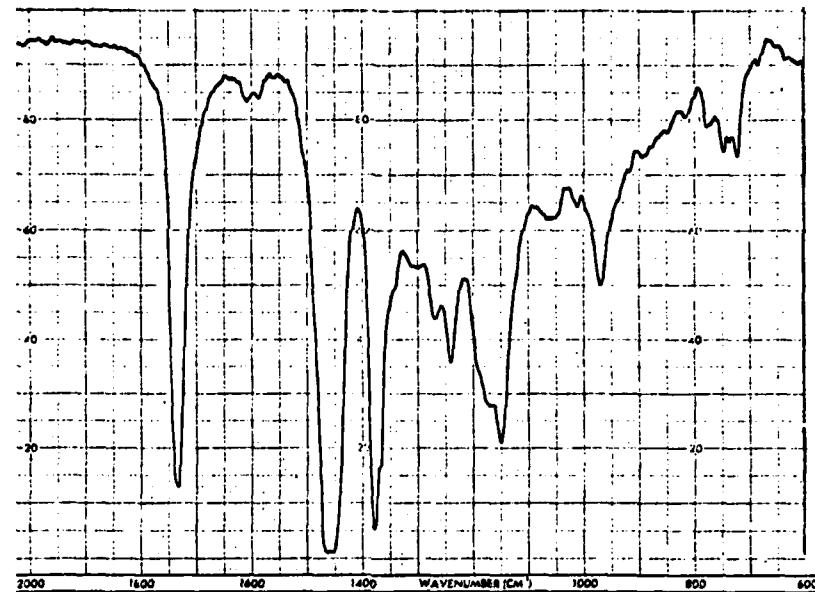


Figure 3. Infrared Spectrum of Hydraulic Fluid

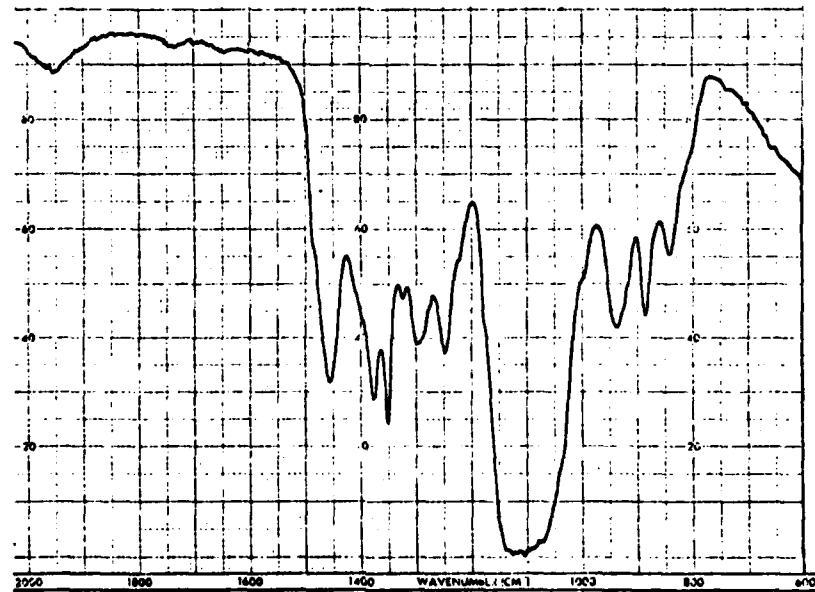


Figure 4. Infrared Spectrum of Brake Fluid



Figure 5. Infrared Spectrum of Solvent Type II

DEVELOPMENT OF THE ANALYTICAL METHOD (continued)

On the basis of the scores, and of the peak intensities, "recognition power" for Diesel Fuel, Hydraulic Fluid, and Brake Fluid was acceptable; for Motor Oil was marginal; and for Solvent Type II was poor. The poor recognition power for Solvent Type II by the absence of unique peaks was further diminished in that the five shared peaks were respectively present in the remaining four products, as shown in Table 1. Consequently, under the procedural conditions used, Solvent Type II would not be identifiable by infrared spectroscopy in a mixture in which the four other hydrocarbon products are present.

This deficiency was remedied by the auxiliary use of gas-liquid chromatography, which has the inherent capability for differentiating between hydrocarbons having similar molecular structure, but differing in some other property.

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Application of Gas-Liquid Chromatography (GLC)

Motor Oil, Diesel Fuel, and Solvent Type II are all related to each other in being fractions obtained from the distillation of petroleum. Petroleum crudes have a predominant component of n-paraffin hydrocarbons in a homologous series of carbon numbers to C₄₀ or more. The chromatogram of a typical petroleum sample is characterized by a periodic sequence of peaks representing unit increments in carbon numbers of the n-paraffin series. Through application of the carbon-number criterion in GLC, differentiation of the lower molecular-weight n-paraffin fractions, which characterize Solvent Type II and Diesel Fuel, from the higher molecular-weight fractions, which constitute motor lubricating oils, can readily be made. The chromatograms subsequently run on Solvent Type II, Diesel Fuel, and 30W Oil (Figure 6) clearly show this differentiation.

Thus, through the complementary capabilities of GLC with IR spectroscopy, recognition of each of the five specific hydrocarbon products in the presence of each other was made possible.

INSTRUMENTAL PROCEDURES

Infrared Spectroscopy

Infrared spectra of reference materials and samples were obtained using a double-beam, optical-null type, microprocessor-controlled infrared spectrophotometer (Perkin Elmer 283B) with operating parameters selected for a nominal resolution of 1 cm⁻¹ in the range between 2000 and 600 wavenumbers. Absorption cells were of the sealed, demountable type, with KBr windows and cell path-lengths of 0.01 and 0.05 mm, dependent on sample type. Replicate transmission spectra were digitally recorded over the range between 2000 and 600 cm⁻¹ at 1-wavenumber sampling intervals through a computer-interfacing system (Perkin-Elmer Data Station). The spectral scans were averaged, and stored on magnetic discs. The retrieved spectra were smoothed with a 13-point quartic smooth (14) prior to generating peak files formatted to print the wave-number and transmittance (or absorbance) of each peak occurring above a given threshold value. The signal-averaged spectra were viewed on a video display by which the necessary transformation of transmittance/absorbance, or accumulation techniques to enhance peak intensity, could be observed. The resulting spectra were then computer plotted on formatted strip charts or on variable computer-generated grids.

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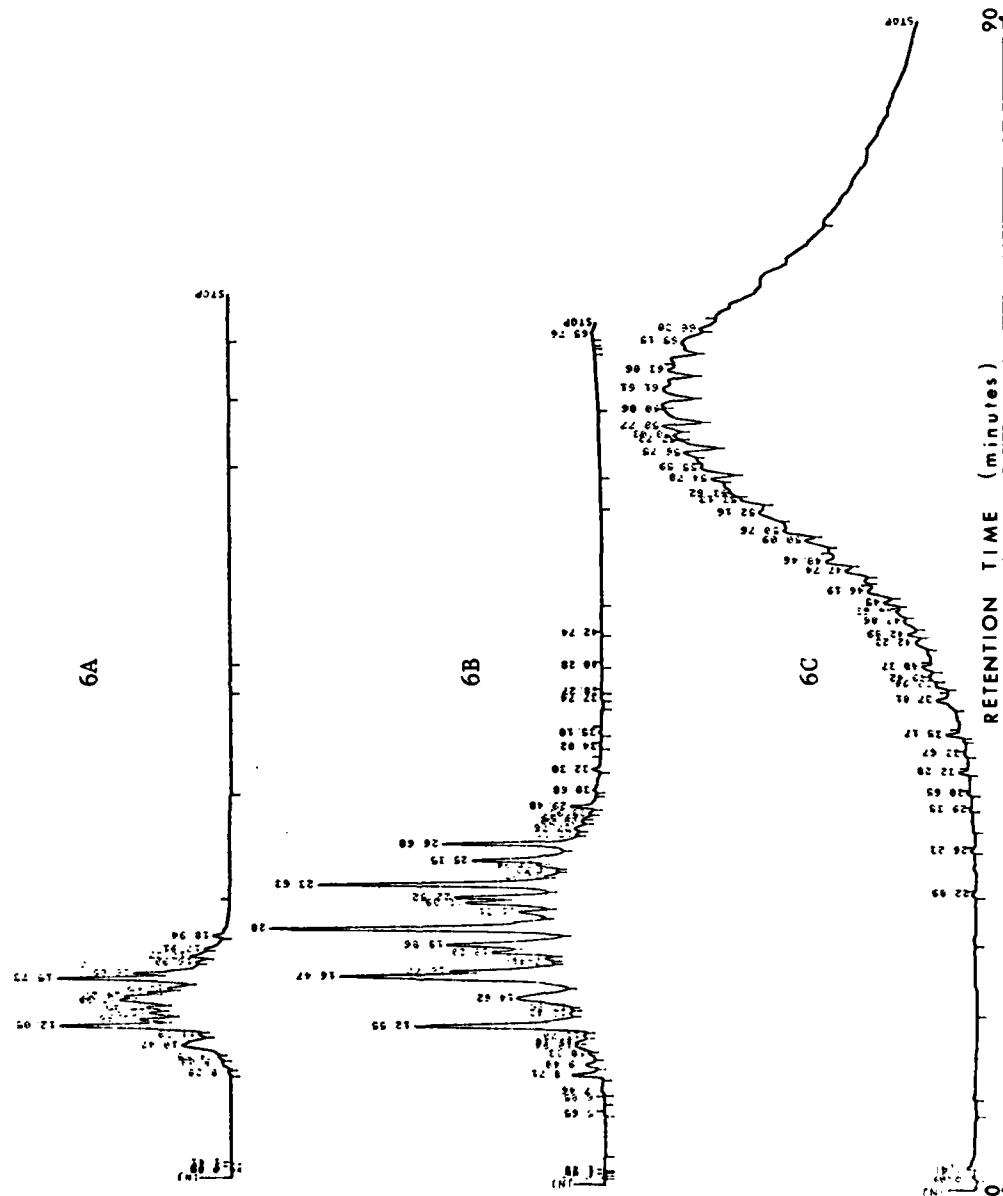


Figure 6. Gas-Liquid Chromatograms of (A) Solvent Type II, (B) Diesel Fuel, (C) 30W Motor Oil

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Gas-Liquid Chromatography

Equipment used in the GLC measurements consisted of a Hewlett-Packard Model 5754 Gas-Liquid Chromatograph equipped with temperature programming and a flame ionization detector. A 6-foot 3.2 mm stainless-steel column was packed with 6% Dexcil 300 on 80/100-mesh Chromasorb WHP. Column temperature was programmed through a linear range between 90° and 325°C at a rate of 4°C per minute. Sample volumes were typically between one and four microliters, depending on sample type. Output signals were processed through a Hewlett-Packard 3380A recording integrator which plotted the chromatogram with retention times indicated at each recorded peak, and also printed a table of the respective peak areas as percent of the total.

Sample Preparation

Reference samples of the hydrocarbon products included in the study were MIL-Spec materials obtained from the Ft. Lewis stores. Hydrocarbon samples received from the field were typically skim samples consisting of an oily phase containing solid debris and occluded water overlaying an aqueous phase. Since water even in trace amounts presents strong spectral interference in the infrared region and etches alkali-halide cell windows, complete separation of the organic phase from the aqueous phase was necessary. This was accomplished on a physical basis by centrifugation of appropriate portions of the sample in 20-ml centrifuge tubes at a temperature of approximately 30°C. A portion of the supernatant organic layer was then carefully drawn off with a Pasteur pipette and transferred to another tube. The cycle was repeated until a clear organic phase was obtained. The separated organic phase was filtered through anhydrous magnesium sulfate, which reduced the remaining traces of water to levels not detected in the recorded spectra.

Conventionally employed solvent extraction of the organics from field samples, followed by evaporation of the solvent, was avoided because of the inevitable addition of interfering solvent peaks if evaporation is performed at low temperatures, and the variable loss of relatively volatile fractions of the sample if the solvent evaporation is conducted at higher temperatures.

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WEATHERING EFFECTS

When oils or other hydrocarbons are discharged in an aqueous effluent and are exposed to the atmosphere as emulsions or films overlaying an aqueous phase, changes in molecular structure occur on a time-related basis from the effects of solar irradiation, temperature, agitation, adsorption on solids, bacterial action, and by chemical interaction with other compounds in the effluent. These changes are reflected in the IR spectra and chromatograms of the materials. This so-called "weathering" must be taken into account in using "off the shelf" standard reference samples of the hydrocarbon products for identification of the same products in a recovered sample that has undergone environmental exposure. The changes that occur in weathered hydrocarbons are reflected in the emergence or increases of the oxidation-related carbonyl bands around 1700 cm^{-1} , increases in some aromatic-related bands, and in a general increase in baseline level in the 600 to 1500 cm^{-1} region.

Numerous techniques to simulate environmental weathering have been developed. The U.S. Coast Guard, the Department of the Interior, the Environmental Protection Agency, and others concerned with the fingerprinting of crude oil and petroleum products in marine and terrestrial environments have devoted considerable R&D effort in studies of the compositional changes due to weathering, and to the development of techniques for simulated weathering of reference samples that takes into account or compensates for the environmental effect (15,16). It has been shown in the reported references that the reliability of analytical fingerprinting methods is improved when synthetically weathered standards are employed in the identification of a recovered crude oil or petroleum product.

Methods developed and adopted by ERDA and ASTM for the synthetic weathering of crude oil involves a distillation under reduced pressure of the suspect and recovered oil samples, and collection of the $+275^\circ\text{C}$ (atm) fraction which is used in the subsequent analysis (16,17). The distillation technique for synthetic weathering of crude oils results in the rejection of the light fractions having n-paraffin carbon numbers of 15 or less. The rejection of the low carbon-number fraction does not affect analytical methods for the fingerprinting of crude oils which usually contain a n-paraffin series extending to C_{40} or more. However, such synthetic weathering methods are unsuited for the synthetic

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weathering of effluent samples containing diesel fuel, solvent, and other light hydrocarbon fractions. Synthetic weathering by long-wavelength ultraviolet irradiation and aeration at temperatures below 40°, as used by Anderson *et al.* (18), offer more appropriate alternatives.

In the weathering procedure adopted for this study, a 10-ml volume of a given MIL-Spec reference hydrocarbon material was added to approximately 30 ml of water contained in a 100-ml beaker, forming a supernatant organic layer of approximately 5 mm overlaying the aqueous layer. The beakers containing the five hydrocarbon products were irradiated by sunlight-simulating fluorescent tubes placed approximately 10 cm above the liquid level in an Atlas UVCOR atmospheric weathering chamber for a period of 48 hours at a temperature of 31°C. The percent change in weight of the reference materials after weathering was calculated.

As would be expected, significant weight losses by evaporation occurred in the light-distillate petroleum materials such as Diesel Fuel (37%) and Solvent Type II (54%). Weight losses from Hydraulic and Brake Fluids were moderate (6-8%), and the 30W Motor Oil showed an insignificant weight loss (less than 0.2%).

A comparison of the infrared spectra of the weathered *vs* not weathered reference materials showed neither emergence of new peaks nor disappearance of existing ones. Spectral changes were limited to slight increases in background absorption in the 1300 to 600 cm^{-1} region; an increase in peak heights of oxidation-related bands around 1700 cm^{-1} , and changes in the peak ratios of the Diesel Fuel absorption bands in the 750 cm^{-1} spectral region. Thus, for the specific hydrocarbon products included in this study, artificial weathering of reference materials did not change the "recognition power" of the selected infrared absorption bands.

Since the weathering of light fractions of the hydrocarbons which constitute Solvent Type II and Diesel Fuel results in significant loss of lower-boiling components, this loss is reflected in attenuation or absence of the lower carbon-number peaks in gas-liquid chromatograms. In GLC techniques, weathering effects must be taken into account in the interpretation of chromatographic data. Reference materials should be artificially weathered before chromatographic comparisons are made with field samples.

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RESULTS

The utility of the tentative infrared/gas-liquid chromatographic analytical method was shown by its ability to successfully identify hydrocarbon products in "known unknowns" prepared from the five hydrocarbon reference materials. In a field sample of wastewater from the Flora Road outfall, Ft. Lewis, Washington, hydrocarbon products identified in the organic phase included motor oil, diesel fuel, and hydraulic fluid. The complementary "recognition powers" of IR and GLC were clearly evident--the marginal capability of IR to recognize motor oil in the presence of the other specified hydrocarbon products was effectively augmented by the strong recognition power of GLC for this material. Diesel fuel was identified by both IR and GLC; hydraulic fluid was readily identified by IR.

CONCLUSIONS

At this stage in the development of a method to identify specified hydrocarbon products in wastewater from vehicular service areas on Army installations, neither infrared spectroscopy nor gas-liquid chromatography, when used alone, completely establishes the identity of all the products in the presence of each other. However, when used in combination, IR/GLC can be the basis of an effective analytical method.

Although a method involving only one analytical discipline would have obvious advantages over one involving, as in this case, both IR and GLC, the advantages would be real only if the total procedural details and instrumentation required in the application of the single discipline would be less complex than through the use of two disciplines in combination. The tentative method described for this specific and limited purpose is relatively simple, and could be used with instrumentation and by personnel typical of the well-equipped analytical laboratory.

ACKNOWLEDGMENT

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